THE AB-INITIO SIMULATION OF THE LIQUID Ga-Se SYSTEM

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(February 8, 2008)

Abstract

Ab-initio dynamical simulation is used to study the liquid Ga-Se system at the three concentrations Ga_2Se, GaSe and Ga_2Se_3 at the temperature 1300 K. The simulations are based on the density functional pseudopotential technique, with the system maintained on the Born-Oppenheimer surface by conjugate gradients minimization. We present results for the partial structure factors and radial distribution functions, which reveal how the liquid structure depends on the composition. Our calculations of the electrical conductivity σ using the Kubo-Greenwood approximation show that σ depends very strongly on the composition. We show how this variation of σ is related to the calculated electronic density of states. Comparisons with recent experimental determinations of the structure and conductivity are also presented.

I. INTRODUCTION

The properties of many binary liquids depend very strongly on the composition (e.g. [1]). We have chosen the metal-selenium systems to study these phenomena. There are experimental measurements showing the very strong and unusual changes in the electronic properties of these systems [1–3]. We use ab-initio molecular dynamics (AIMD) to study

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the liquid structure and the relation between this structure and the electronic properties. In this paper we report results for the liquid Ga-Se system (Ag-Se is discussed in a separate paper [4]). This mixture of a good metal (gallium) and a poorly conducting material (selenium) enables us to study the changes in the electronic properties when we go from a metallic system to an insulating one. In order to have a complete picture of the changes in this system we have also performed simulations on the pure liquid elements Ga [5] and Se [6]. The ab-initio approach allows us to study simultaneously the structure and the electronic properties, and our calculations are free from any assumptions about the form of the interatomic interaction (for other AIMD work on liquids, see e.g. refs. [7–11]). There are no experimental data for the liquid Ga-Se system published so far, but we shall present a comparison with preliminary data from the Bristol group [12].

II. TECHNIQUE

Our ab-initio molecular dynamics method is based on the Car-Parrinello approach [13], but instead of using 'fake dynamics' we bring the system to the Born-Oppenheimer surface at every ionic configuration using conjugate gradients minimisation. We deal with the semimetallic character of our system by treating the occupation numbers as additional variables. The details of our method are described elsewhere [4,5]. Once the electronic ground states is reached, the quantum forces are calculated; we can then apply the standard algorithm of classical molecular dynamics.

The ab-initio simulations are very computationally demanding and, even when using supercomputers, there are very strong limitations on the size of the system and the length of the simulations. We use 60 atoms in a cubic box with the periodic boundary conditions. We have performed calculations for three concentrations, namely Ga_2Se (40 Ga atoms and 20 Se atoms), GaSe (30 Ga atoms and 30 Se atoms) and Ga_2Se_3 (24 Ga atoms and 36 Se atoms). The calculations were done at densities interpolated between pure Ga and pure Se (such a simple interpolation at room temperature predicts densities of solid GaSe and

Ga_2Se_3 within a few percent).

We use non-local pseudopotentials and a plane-wave cut-off of 150 eV, with only the gamma point used to sample the Brillouin zone. All simulations were done at the temperature 1300 K. The integration time-step for the ion dynamics was 3 fs, and we equilibrated our system (at each concentration) for over 1 ps and the ensemble averages were calculated from the next 4 ps.

III. RESULTS

A. Structural properties

In Figure 1 we compare our neutron weighted structure factors with preliminary experimental results [12]. Our structure factors were calculated directly in k-space so the resolution for small k is very low and the noise is substantial. The agreement is reasonably good: the positions of the peaks are correct and the general dependence of peak heights on concentration is also reproduced correctly. There is some disagreement in peak heights, especially for Ga_2Se, but one should bear in mind the small size of our system.

It is very useful to analyse changes in the partial structure factors and the radial distribution functions even though we do not have the experimental results to compare with. In figure 2 we show the partial Faber-Ziman structure factors together with the total structure factor for all three concentrations in the region of the first peaks. One can see that the structure of the partial $S(k)$ is much richer than of the total one but there is a high degree of cancellation of the peaks (the partial structure factors contribute to the total one with the different prefactors). The variation in the height of the peak at about 2 Å^{-1} can be traced to changes in the degree of cancellation of the Se-Se and Ga-Se partials at this k-vector.

The partial radial distribution functions can be calculated directly in real space. In Figure 3 we show the partial radial distribution functions and their evolution with increasing concentration of selenium. All of them change markedly. In the Ga-Ga rdf a peak appears

at about 2.45 Å. In Ga_2Se and GaSe, the Se atoms are well separated and the first peak in the rdf is at just below 4 Å. For Ga_2Se_3 we see a clear peak at about 2.45 Å (there is a very small peak at this position for GaSe). This distance corresponds to the Se-Se distance in pure liquid and solid selenium. On average there are four Se-Se bonds in our system at this concentration. This number is low because we are at the stoichiometric concentration. We also observe the growth of the first (and only) peak in the Ga-Se rdf.

As a useful characterization of our rdf results, we show in Table 1 the average coordination number of different types of atoms corresponding to a cutoff of 3 Å.

B. Electronic properties

The electronic densities of states (together with the results for pure gallium at 1000 K) are compared in Figure 4. The changes in the electronic density of states are substantial. We start from the almost free-electron like behaviour for pure gallium and end up with a gap for Ga_2Se_3. This is a real gap in the density of states, and not just a pseudo-gap or a conduction gap. Interestingly, we found that we had to run the simulations for a few picoseconds before the gap opened. During this long equilibration the radial distribution function remained the same while we saw a steady changes in the energy eigenvalues. With increasing concentration of selenium, a large peak builds up between -15 eV and -10 eV. These are s states of selenium. A detailed analysis of the electronic density of states, localization of electrons and the pseudo-charge distribution will be published elsewhere [14].

Given the major variations of the density of states, it is not surprising to find that the electrical conductivity changes dramatically with the concentration. We calculated the d.c. conductivities using the Kubo-Greenwood formula for the a.c. conductivity $\sigma(\omega)$ and by extrapolating this to $\omega = 0$. There are many approximations involved so one does not expect perfect agreement with experiment. For pure gallium the calculated conductivity is 20 000 $\Omega^{-1}cm^{-1}$, for Ga_2Se it is about 1000 $\Omega^{-1}cm^{-1}$, for GaSe this value drops down to about 100 $\Omega^{-1}cm^{-1}$ and for Ga_2Se_3 it is almost zero. The corresponding experimental

values are: 28 000 [15], 1000, 25 and 3 Ω^{-1}cm^{-1} [12].

IV. CONCLUSIONS

The main conclusions are as follows. The reasonable agreement of our calculated neutron-weighted structure factors with preliminary experimental results confirms the reliability of our AIMD simulations. Our study of the partial structure factors shows that the form of the neutron-weighted structure factor involves a large degree of cancellation between features in the partials. The rdfs reveal that at low Se concentrations, the Se atoms are well separated from each other, but at the Ga_2Se_3 composition the formation of Se-Se short-distance bonds plays a significant role. The electronic density of states varies strongly with composition, and increase of Se content causes the opening of a true gap at the Fermi level.

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FIGURES

FIG. 1. The neutron weighted structure factor $S(k)$ of Ga_2Se , GaSe and Ga_2Se_3. Solid line and circles connected by dotted line represent simulation and experimental values [12] respectively. Data for Ga_2Se are shifted up 0.5 mb/atom, for Ga_2Se_3 down by 0.5 mb/atom.

FIG. 2. The partial Faber-Ziman structure factors and the total structure factor for three concentrations of Ga-Se.

FIG. 3. The partial radial distribution functions for three concentrations of Ga-Se.

FIG. 4. Electronic density of states for pure liquid gallium, Ga_2Se, GaSe and Ga_2Se_3.

TABLE I. The average coordination numbers for Ga-Se alloys and positions of the first peaks in the radial distribution fuction, in brackets the interatomic distances and the coordination numbers of the corresponding solid phase. Distances in Å.

alloy	r_{Ga-Ga}	n_{Ga-Ga}	r_{Ga-Se}	n_{Ga-Se}	n_{Se-Ga}	r_{Se-Se}	n_{Se-Se}
Ga_2Se	2.54	2.41	2.44	1.46	2.92	3.95	0.01
GaSe	2.51 (2.44)	1.12 (1)	2.44 (2.45)	2.66 (3)	2.66 (3)	3.95 (4.75)	0.02 (0)
Ga_2Se_3	2.46 (3.85)	0.62 (0)	2.43 (2.35)	3.39 (4)	2.26 (2.67)	3.95 (3.85)	0.30 (0)